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STUDY OF CORROSION SPECIES AND INHIBITORS ON ALUMINUM BY INELAS--ETC(U)

DEC 80 H W WHITE, T WOLFRAM

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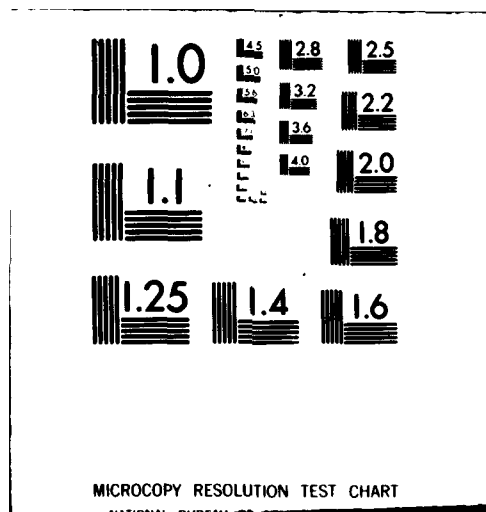
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>The technique of Inelastic Electron Tunneling Spectroscopy (IETS) has been applied to the study of corrosion and inhibition of corrosion of aluminum in the presence of organics. IETS spectra were measured and analyzed to obtain information on the intermediate and final corrosion species formed during the reaction of several chlorinated hydrocarbons with aluminum oxide surfaces. This information was coupled with previous corrosion and reaction results. |                                     |   |

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to develop reaction sequences and formulate corrosion mechanisms on a microscopic basis. Carbon tetrachloride and trichloroethylene were studied in detail. Studies on the inhibitor formamide provided information on the surface species formed, its orientation, and the types of sites with which it reacted. A comparison of experimental and theoretical intensities for formic acid adsorbed on aluminum was made in an attempt to make IETS a more quantitative tool for these kinds of studies. Model calculation for corrosion reaction mechanisms were also made and reported.

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**TITLE**

**Study of Corrosion Species and Inhibitors on Aluminum by Inelastic Electron  
Tunneling Spectroscopy**

**TYPE OF REPORT (TECHNICAL, FINAL, ETC.)**

**Final**

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## I. PROBLEMS STUDIED

Information on the intermediate and final corrosion species produced at the surface of a metal would be an important aid in the development of corrosion mechanisms. The characterization on a molecular scale of the processes occurring at a metal electrolyte interface is difficult since the thickness of the interface region is of the order of 10 to 100 angstroms. Inelastic Electron Tunneling Spectroscopy (IETS) was used to study the basic mechanisms of corrosion and inhibition for several important aluminum corrosion problems involving organics. These efforts were directed at development of the understanding of the corrosion and toward effective means to design more corrosion resistant systems. IETS was used to determine the molecular species present at the microscopic interface between an aluminum oxide surface and reactive organics. The measurements were made on tunneling junctions fabricated with several commercially important chlorinated hydrocarbons. The surface species for a number of molecules used as inhibitors for these systems were also studied. The work in our laboratory under this program has demonstrated IETS to be an effective technique for the study of corrosion reactions and inhibitor mechanisms on aluminum.

## II. SUMMARY OF RESULTS

IETS provides a versatile and sensitive method for measuring the vibrational spectrum of a molecular species adsorbed on the surface of an insulating metal oxide. It involves the measurement of the electric current  $I$  associated with electrons which tunnel through an oxide film having an adsorbed molecular layer on its surface. The electrons, which inelastically tunnel through the oxide, excite the characteristic vibrations of the adsorbed molecules. The spectra show peaks which can be associated with the presence of both infrared and Raman-like modes. The spectra can be used to identify molecular species on the oxide layer, estimate molecular orientation, and detect chemisorption bonding to the oxide layer.

The molecular species to be studied is placed in contact with an oxidized metal film. Another metallic film (usually lead) is evaporated over the "doped" oxide to form a metal-insulator-metal tunnel junction. The junction is then cooled to liquid helium temperatures and the spectra measured. One of the primary advantages of IETS over other spectroscopic techniques for the study of corrosion is its sensitivity. Coverages of a monolayer or less can easily be studied. Its main disadvantages are that the preparation of good samples free of unwanted contamination is not easy and that liquid helium temperatures are required for good resolution.

IETS spectra were measured and analyzed to obtain information on the chemical species formed during reaction of selected organics with aluminum oxide surfaces. This information was coupled with previous corrosion and reaction information to develop reaction sequences and to formulate corrosion mechanisms on a microscopic basis. Of particular interest was the type of surface sites which play an important role in the initiation of the reactions. The design of effective inhibitors and of more corrosion resistant alloys depends critically on the nature of these sites and how they are affected by the presence of other metal atoms and chemicals

species either on, or incorporated into, the oxide layer. Pure aluminum was used for these studies.

The results for several completed projects are given in the following sections.

1. Corrosion Reactions: IETS was used to determine the molecular species which occur on an aluminum oxide surface during metallic corrosion by carbon tetrachloride. IETS spectra were obtained for  $\text{CCl}_4$  adsorbed on aluminum oxide, and the observed vibrational modes were assigned by comparison with infrared and Raman frequencies. Modes were observed which could be associated with the molecular species  $\text{CCl}_4$ ,  $\text{AlCl}$ ,  $\text{AlCl}_2$ ,  $\text{AlCl}_3$ , and  $\text{C}_2\text{Cl}_6$ . The fact that no modes were observed which would reflect oxygen-carbon bonding, and the presence of a large number of aluminum-chlorine modes suggest that the corrosion mechanism is by reaction of the solvent with exposed aluminum atoms. These exposed sites could occur at oxygen vacancies and other imperfections such as grain boundaries. The fact that intermediate species could be detected attests to the sensitivity of IETS. (See Pub. No. 1, Section III).

Similar studies on metallic corrosion by trichloroethylene were also made. The results indicated that the corrosive attack occurs by a two step mechanism which could account for the fact that the corrosion rate of aluminum by trichloroethylene is lower than that of carbon tetrachloride which occurs by direct chemical attack. A reaction sequence was developed which was consistent with the observed aluminum ethoxide type species which was indicated by the IETS results. (Pub. No.3).

2. Inhibitor Mechanisms: We have also determined the molecular species formed on aluminum oxide exposed to the corrosion inhibitor formamide. Small concentrations of formamide are known to inhibit the corrosion of aluminum by carbon tetrachloride. IETS spectra were obtained for formamide and its deuteroderivatives, and for dilute solutions of formamide in carbon tetrachloride. The spectra showed that formamide in the presence of carbon tetrachloride was preferentially adsorbed on the aluminum oxide surface via the nitrogen bond. The results indicated that the formamide surface species were chemisorbed at oxygen vacancy sites which have exposed aluminum atoms. A model was developed to describe the interaction of the formamide molecule with the oxide surface and to show how the formation of the formamide surface species could inhibit the corrosion of aluminum by carbon tetrachloride. (Pub. No. 2).

3. Development of IETS: In order to develop IETS into a more quantitative tool the theoretical and experimental inelastic electron tunneling intensities were compared for several modes of formic acid adsorbed on aluminum oxide. Several of the proposed theoretical models and calculated results were reviewed. Calibrated spectra for formic acid and its deuterated forms were measured and the vibrational modes identified. The spectra indicated that formic acid adsorbs on alumina as a formate ion. The experimental peak intensities from the undeuterated formic acid spectrum were compared with theoretical intensities calculated using the partial charge model. The intensities were calculated for two orientations of the formate ion--with the C-O bond perpendicular to, and parallel to, the oxide surface. Comparison of the theoretical and experimental intensities for the C-O and C=O modes indicated that the formate ion is oriented perpendicular to the oxide surface. Experimental intensities for modes involving hydrogen were not in good agreement with those obtained from the partial charge calculations. The differences were not unexpected

due to the charge distortion along the C-H bond. The results for modes involving hydrogen indicated that a more sophisticated model than the partial charge model will be required for accurate intensity calculations for C-H modes. (Pub. No.4).

4. Bifurcation Structures: An analysis of the steady state bifurcation structures present in the anodic polarization curves of aluminum identified two significant constraints for any viable model of the anodic corrosion process. These constraints appear in the form of the k-determinacy and codimension of the experimentally observed butterfly catastrophe surface for the anodic region of the polarization surface. Using these constraints it is shown that the "Tafel Law" model of corrosion cannot adequately describe the underlying anodic corrosion chemistry. (Pub. No. 5).

5. Surface Reaction Processes: The steady state surface reaction rate for electrochemical reactions is frequently measured by the polarization curve. In the anodic region of this curve the dynamics of the reaction process are generally described by a semiflow map. The fixed points of this map describe the steady state dynamics of the surface reaction. These generic singularities have been classified according to their bifurcation structure. For the corrosion of aluminum this steady state bifurcation structure is found experimentally to be given by a butterfly catastrophe surface. Each structure has a characteristic signature which can be experimentally observed. This is most readily seen in the polarizations curves obtained in the study of surface reactions in electrochemistry and corrosion. The experimental results constrain the possible physical models that can be considered to describe the reaction process because the codimension and k-determinacy values must agree for both the experiment results and the physical model. In the study of electrochemical corrosion reactions this analysis completely explains why the usual Tafel Law and its associated model of the surface reactions involved is entirely inadequate to describe the physics of the anodic region of the polarization curve. Results of this analysis as applied to electrochemical reaction studies of aluminum are described. (Pub. No. 6).

### III. LIST OF PUBLICATIONS

1. "Study of the Corrosion of Aluminum by  $\text{CCl}_4$  Using Inelastic Electron Tunneling Spectroscopy," R.M. Elliatoglu, H.W. White, L.M. Goodwin and T. Wolfram, J. Chem. Phys. 72, 5291 (1980).
2. "Study of the Corrosion Inhibitors Formamide in the Aluminum-Carbon Tetrachloride System Using IETS," R.M. Elliatoglu, H.W. White, L.M. Godwin and T. Wolfram, J. Chem. Phys. (in press),



3. "Study of the Corrosion of Aluminum by Trichloroethylene using Inelastic Electron Tunneling Spectroscopy," H.W. White and R.M. Elliatiglu and J.E. Bauman Jr., J. Chem. Phys. (in press).
4. "Comparison of Experimental and Theoretical Inelastic Tunneling Spectra for Formic Acid", L.M. Godwin, H.W. White and R.E. Elliatiglu, Phys. Rev. B1 (in press).
5. "Bifurcation Structures: Constraints for Models of Anodic Corrosion Chemistry," by D.G. Retzloff, B. DeFacio, J.E. Bauman, and P.H. Ragatz, Intern'l J. of Engineering (in press).
6. "The Relationship of the Geometry of the Observed Steady State Chemical Conversion Rate to the Basic Surface Reaction Process in Electrochemistry", D.G. Retzloff, B. DeFacio, J.E. Bauman and P.H. Ragatz, AIP Proceedings on Physics of Surfaces (1980) pp. 319-331.

IV. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGRESS EARNED WHILE ON PROJECTS:

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